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# SOLID-STATE DECOMPOSITION STUDIES ON FLUOROPEROXO SPECIES OF TRANSITION METALS. PART III. KINETICS OF ISOTHERMAL DECOMPOSITION OF THE SOLIDS $Rb_3Zr_2(O_2)_2F_7 \cdot H_2O$ AND $Cs_3Zr_2(O_2)_2F_7 \cdot 2\,H_2O$

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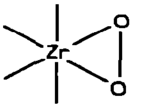
## ABSTRACT

The kinetics of isothermal decomposition of the solids $Rb_3Zr_2(O_2)_2F_7 \cdot H_2O$ and $Cs_3Zr_2(O_2)_2F_7 \cdot 2\,H_2O$, have been studied under vacuum in the temperature ranges 121—200°C and 101—201°C, respectively. The fractional decomposition $\alpha$ has been determined by measuring the pressure of the evolved oxygen during pyrolysis with the help of a McLeod gauge. The $\alpha$ values ranged from 0.14 to 0.79 for $Rb_3Zr_2(O_2)_2F_7 \cdot H_2O$, and from 0.11 to 0.93 for $Cs_3Zr_2(O_2)_2F_7 \cdot 2\,H_2O$. The $\alpha$—time data of both compounds showed that the kinetics are deceleratory throughout the course of the decomposition reaction. In both compounds, the initial stages of the decomposition can be best described by a unimolecular decay law, while the later stages obey contracting-volume kinetics at all temperatures. The activation energies have been determined by Arrhenius plots and the respective values are 13.1 and 9.7 kcal mol$^{-1}$ for $Rb_3Zr_2(O_2)_2F_7 \cdot H_2O$, and 14.4 and 10.9 kcal mol$^{-1}$ for $Cs_3Zr_2(O_2)_2F_7 \cdot 2\,H_2O$. The first step in the peroxide decomposition in these solids may be attributed to the breaking of the metal peroxide bond and consequent release of the strain in the



system, and also to low activation energies ($E_a$) which facilitate nucleation and rapid transport of oxygen through the pores developed due to the loss of lattice water before the onset of the decomposition.

## INTRODUCTION

Solid-state decomposition kinetics [1—5] continue to attract attention even today. The recent review article by Galwey [6] shows that very little work has been done on the solid inorganic peroxy salts which are finding applications in a variety of industries due to the oxygen which they readily release either on heating or on chemical treatment. Vol'nov [7,8], while discussing the present position and possible directions for future investigations of the inorganic peroxide compounds, emphasizes that the areas of kinetics, thermodynamics, mechanistic and structural properties of peroxide compounds require a great deal of further study. Only a few solids, such as

$Li_2O_2$, $Na_2O_2$, $CaO_2$ and $BaO_2$ [9], $Rb_2CO_3 \cdot 3\,H_2O_2$ and $Cs_2CO_3 \cdot 3\,H_2O_2$ [10], and $Na_2C_2O_6$ and $K_2C_2O_6$ [11], have been studied by isotopic measurement of the oxygen evolved. A rigorous mechanism for the liberation of oxygen during the thermal decomposition of inorganic peroxo compounds is yet to be worked out [12]. The kinetic study, though not sufficient in itself, is the first important step in this direction [6].

A continuing programme of work in this laboratory, on the decomposition of zinc azides and zinc hydroxy azides [13], and also on the peroxide chemistry of transition elements [14—17], prompted us to undertake kinetic studies of the decomposition of solid peroxo compounds. It has been observed that fluoroperoxozirconates of alkali metals, $M_3Zr_2(O_2)_2F_7 \cdot x\,H_2O$, are well suited for such studies as they undergo a neat decomposition, giving oxygen, oxofluorozirconate, $M_3Zr_2O_2F_7$ (a stable species) and water vapour which can be condensed in a liquid air trap. The decomposition is of the type

$$A(s) \rightarrow B(s) + C(g)$$

and can be easily studied using the constant-volume apparatus previously reported [18,19]. Further, these solids also undergo photodecomposition; this reaction has also been investigated and the results will be published in a future paper. Hence these compounds are interesting for solid-state decomposition studies.

In the present communication, data on the thermal decomposition of the compounds $M_3Zr_2(O_2)_2F_7 \cdot x\,H_2O$ ($M = Rb^+$, $x = 1$; $M = Cs^+$, $x = 2$) under isothermal conditions are presented and disussed.

## EXPERIMENTAL

### *Materials*

The following reagents were used: Zirconium oxychloride octahydrate, $ZrOCl_2 \cdot 8\,H_2O$ (A.R. grade, Riedel); hydrogen peroxide 30%, $H_2O_2$ (L.R., I.D.P.L.); caesium fluoride, CsF (A.R. grade, Merck); rubidium carbonate, $Rb_2CO_3$ (A.R. grade, Merck); hydrofluoric acid 40%, HF (G.R., Merck); and methanol, $CH_3OH$ (A.R., I.D.P.L.).

### *Sample preparation*

The compounds $Rb_3Zr_2(O_2)_2F_7 \cdot H_2O$ and $Cs_3Zr_2(O_2)_2F_7 \cdot 2\,H_2O$ were prepared by the method reported by Santhamma [20]. A known amount of zirconium oxychloride octahydrate was dissolved in 100 ml of a 1 : 1 mixture of water and methanol. To this solution about 30 ml of 30% hydrogen peroxide was added with stirring. This was followed by slow addition of caesium fluoride or rubidium fluoride in the appropriate quantity to maintain the zirconium : fluoride mole ratio at 1 : 7 (rubidium fluoride was prepared by reacting the rubidium carbonate with hydrofluoric acid). A white solid, which precipitated immediately, was allowed to remain in contact with the mother liquor for some time. It was separated by filtration, washed thoroughly with a 1 : 1 mixture of water and methanol, and finally washed with acetone. The compound was ground and dried over phosphorus pentoxide and analyzed. The sample was homogenized by sieving below 150 mesh.

### *Equipment*

The set-up of the apparatus was the same as previously reported [18,19]. It had a constant-volume system fitted with a McLeod gauge. The system containing the sample was evacuated to a pressure of $10^{-6}$ torr. The sample was heated at the desired temperature to within ±0.25° C by an electronically controlled furnace. The condensable water vapour evolved was removed by using a liquid-air trap. The fractional decomposition $\alpha$ was determined by measuring the pressure of oxygen evolved at different time intervals.

## RESULTS

### $Rb_3Zr_2(O_2)_2F_7 \cdot H_2O$

The isothermal decomposition of the compound was carried out in the temperature range 121—200° C. The primary kinetic data ($\alpha$—time) thus obtained are presented in Fig. 1, which shows that there is no induction period and acceleratory region as generally observed in solid-state decomposition

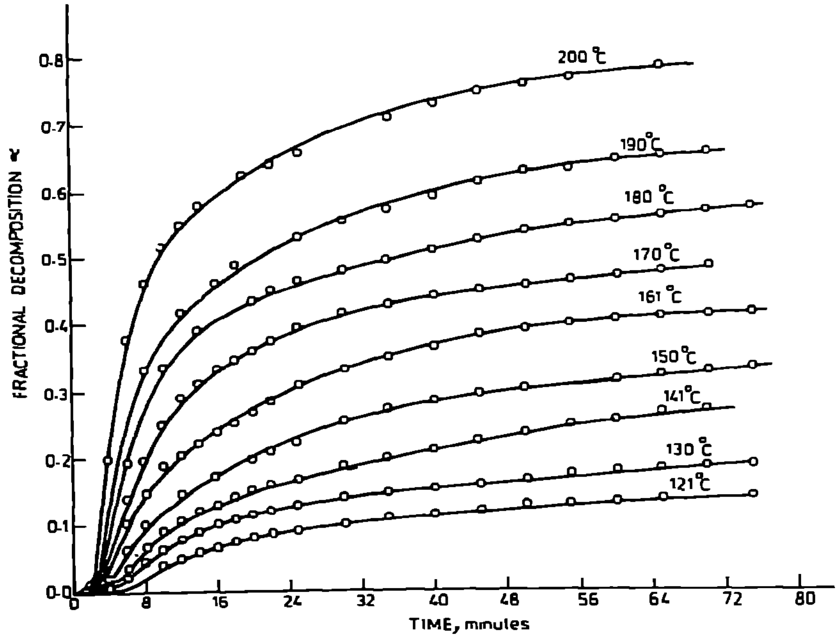


Fig. 1. Thermal decomposition curves of rubidium fluoroperoxozirconate, $Rb_3Zr_2(O_2)_2F_7 \cdot H_2O$, at different temperatures.

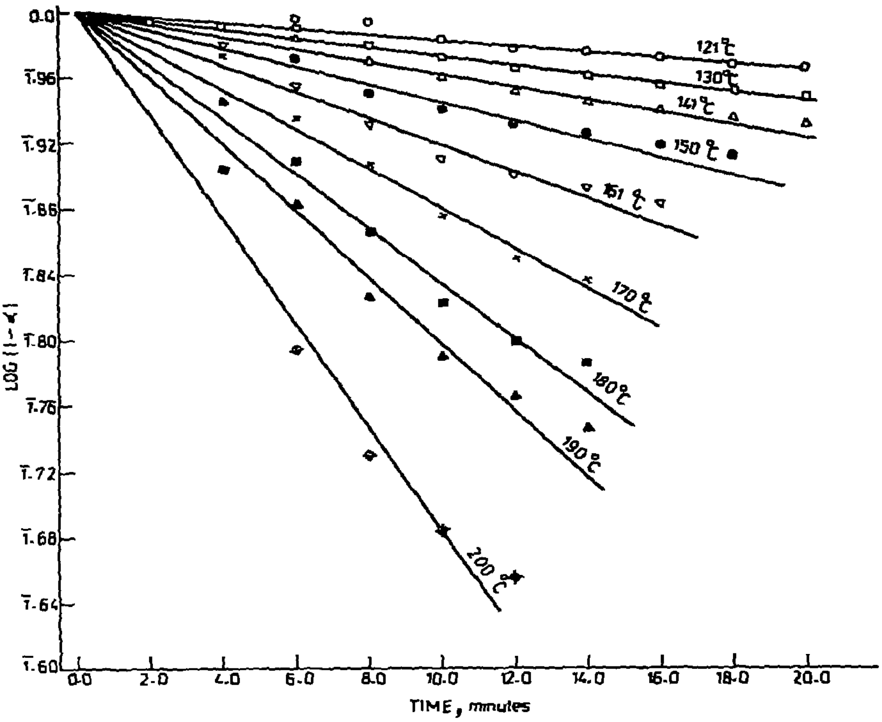


Fig. 2. Plot of log(1 — α) vs. $t$, unimolecular decay law for rubidium fluoroperoxozirconate, $Rb_3Zr_2(O_2)_2F_7 \cdot H_2O$.

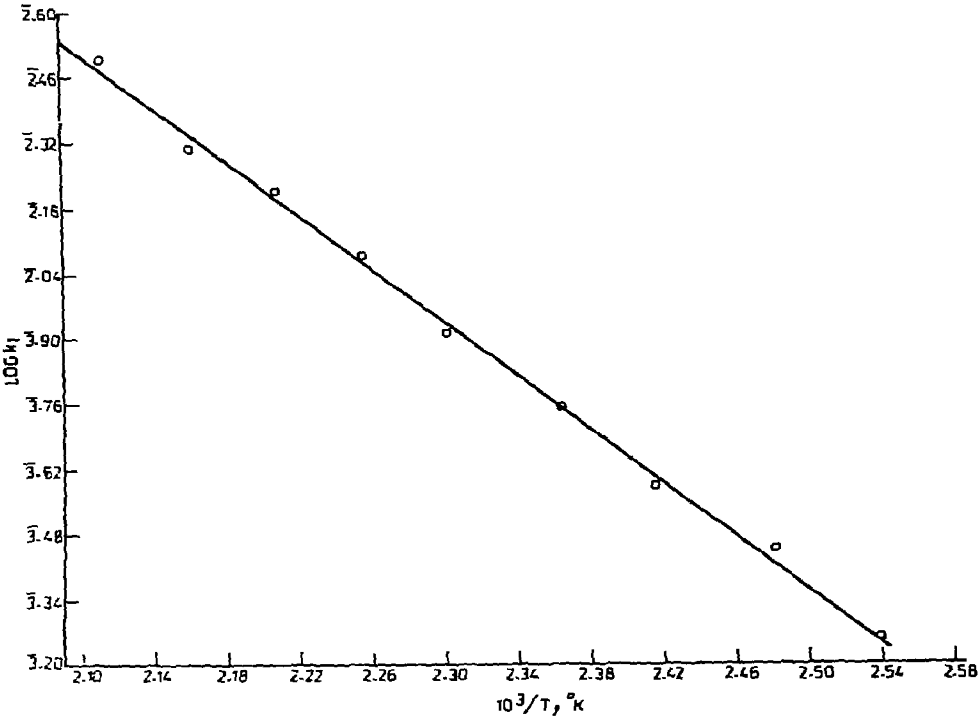


Fig. 3. Arrhenius plot of unimolecular decay law rate constants, i.e. log $k_1$ vs. $1/T \times 10^3$ (K).

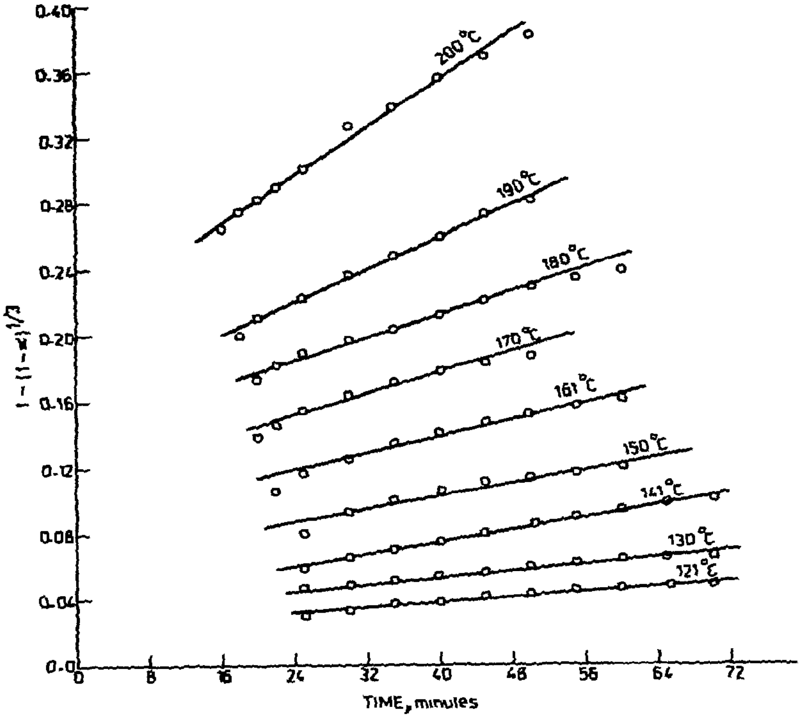


Fig. 4. Plot of $1-(1-\alpha)^{1/3}$ vs. $t$, contracting-volume equation, for rubidium fluoroperoxozirconate, $Rb_3Zr_2(O_2)_2F_7 \cdot H_2O$.

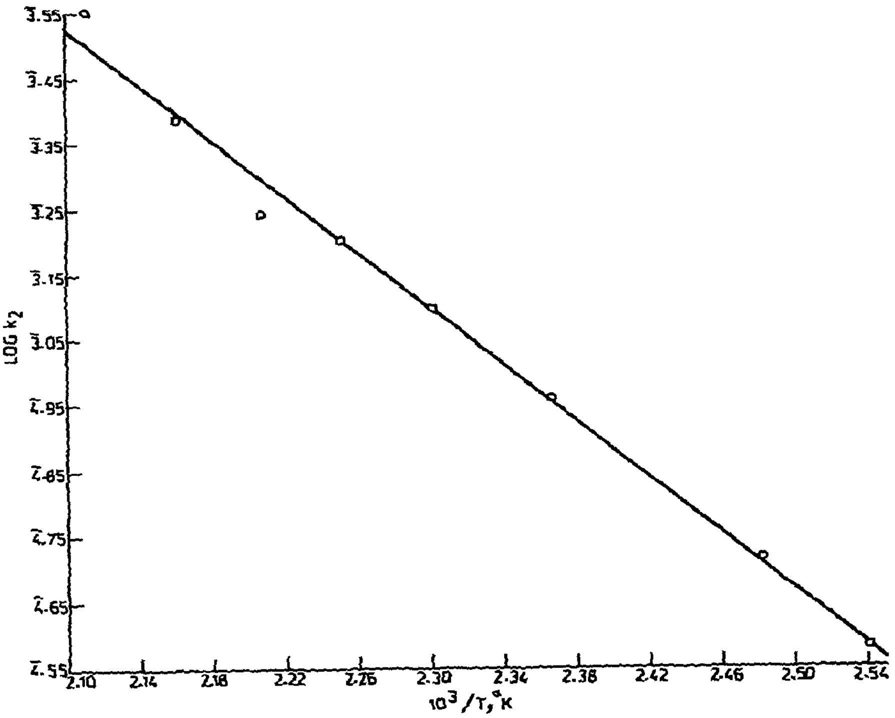


Fig. 5. Arrhenius plot of contracting-volume rate constants, i.e. log $k_2$ vs. $1/T \times 10^3$ (K).

studies. At all temperatures, the compound decomposes at a maximum rate at the beginning of the reaction; the rate subsequently decreases with increasing degree of decomposition, i.e., the reaction is deceleratory throughout the course of the decomposition. The minimum and maximum values of $\alpha$ obtained in this temperature range are 0.14 and 0.79, respectively.

The various kinetic equations [21] commonly used to describe the thermal decomposition of solids were tried. The entire decomposition range could not be explained by using a single rate equation. The initial part of the decomposition can be best described by a unimolecular decay law (Fig. 2). The rate constants were calculated at different temperatures, and thereafter the activation energy was determined by an Arrhenius plot (Fig. 3); the value of $E_a$ is 13.1 kcal mol$^{-1}$. The later stages of the decomposition can best be explained by the contracting-volume equation (Fig. 4). Similarly, the rate constants were calculated at various temperatures, and thereafter the activation energy was determined, from an Arrhenius plot, to be 9.7 kcal mol$^{-1}$ (Fig. 5).

### $Cs_3Zr_2(O_2)_2F_7 \cdot 2\,H_2O$

The decomposition of solid $Cs_3Zr_2(O_2)_2F_7 \cdot 2\,H_2O$ was studied under isothermal conditions in the temperature range 101—201° C. The primary $\alpha$—time data is plotted in Fig. 6. The nature of the $\alpha$—time plots is similar to those of the rubidium analogue. The rate of decomposition is at a maximum

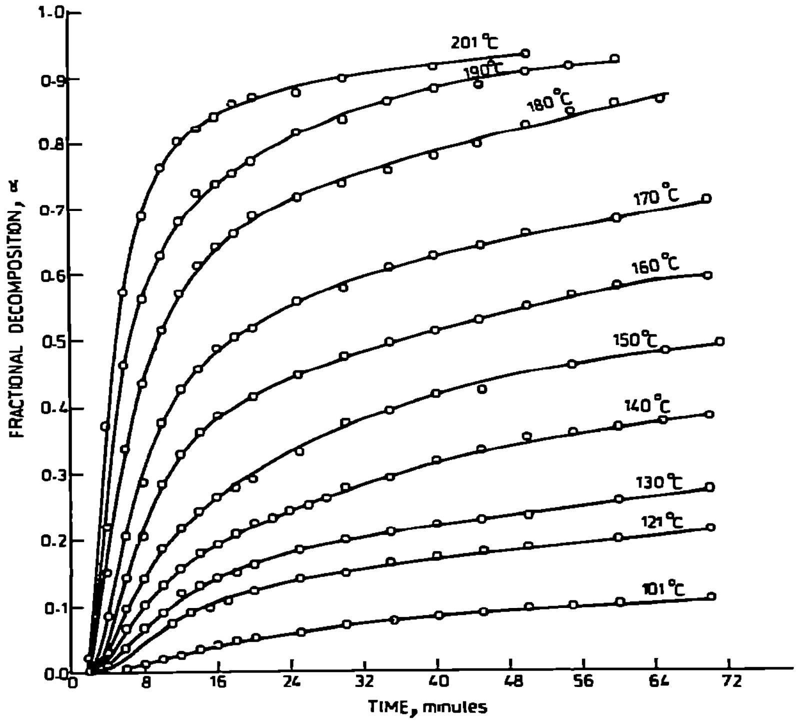


Fig. 6. Thermal decomposition curves of caesium fluoroperoxozirconate, $Cs_3Zr_2(O_2)_2F_7 \cdot 2\,H_2O$, at different temperatures.

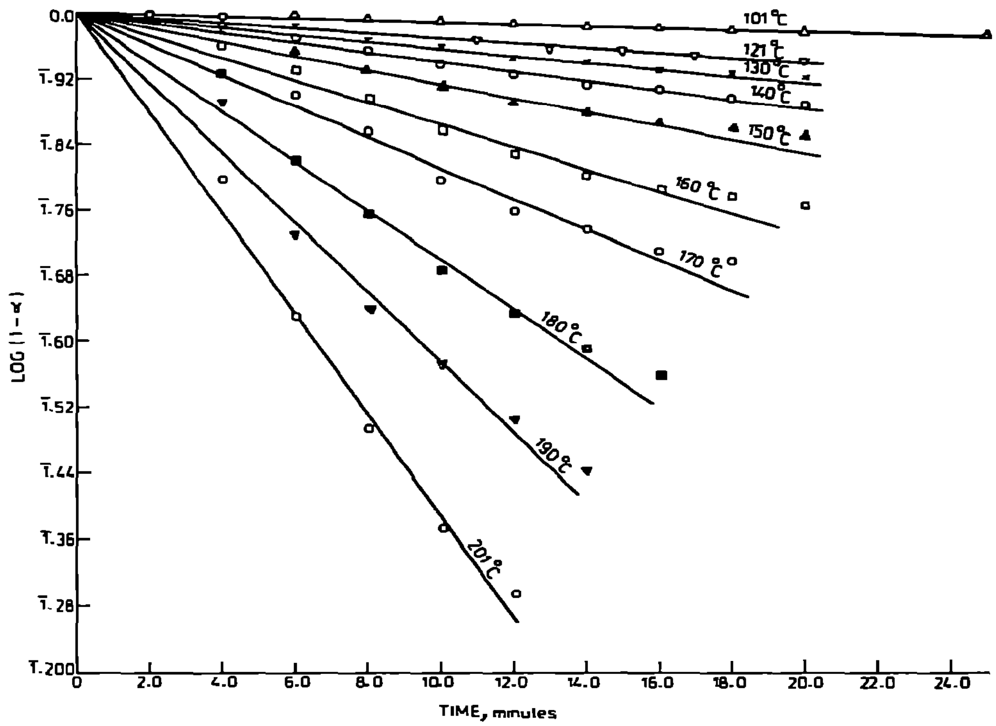


Fig. 7. Plot of log(1 — α) vs. *t*, unimolecular decay law for caesium fluoroperoxozirconate, $Cs_3Zr_2(O_2)_2F_7 \cdot 2\ H_2O$.

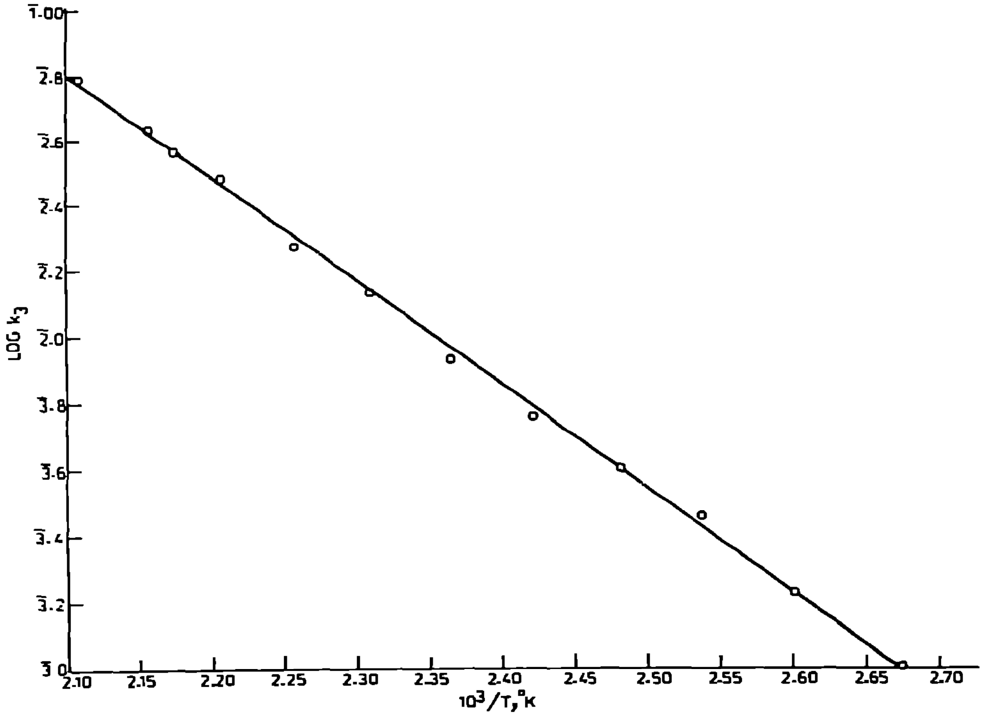


Fig. 8. Arrhenius plot of unimolecular decay law rate constants, i.e. log $k_3$ vs. $1/T \times 10^3$ (K).

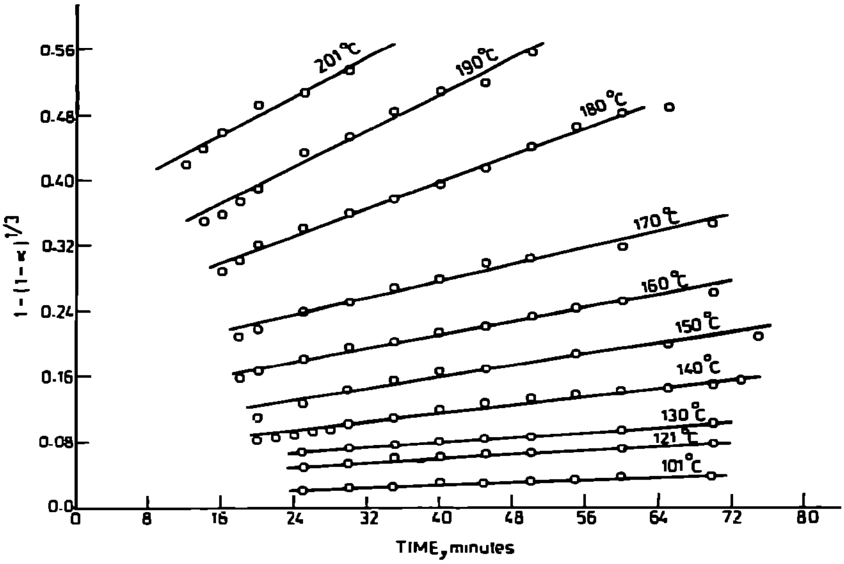


Fig. 9. Plot of $1-(1-\alpha)^{1/3}$ vs. $t$, contracting-volume equation for caesium fluoroperoxozirconate, $Cs_3Zr_2(O_2)_2F_7 \cdot 2\,H_2O$.

at the beginning of the reaction; thereafter the rate decreases. The minimum and maximum values of $\alpha$ obtained in this temperature range are 0.11 and 0.93, respectively.

As in the case of the rubidium compound, the entire decomposition range could not be described by a single rate equation. The initial stage of the

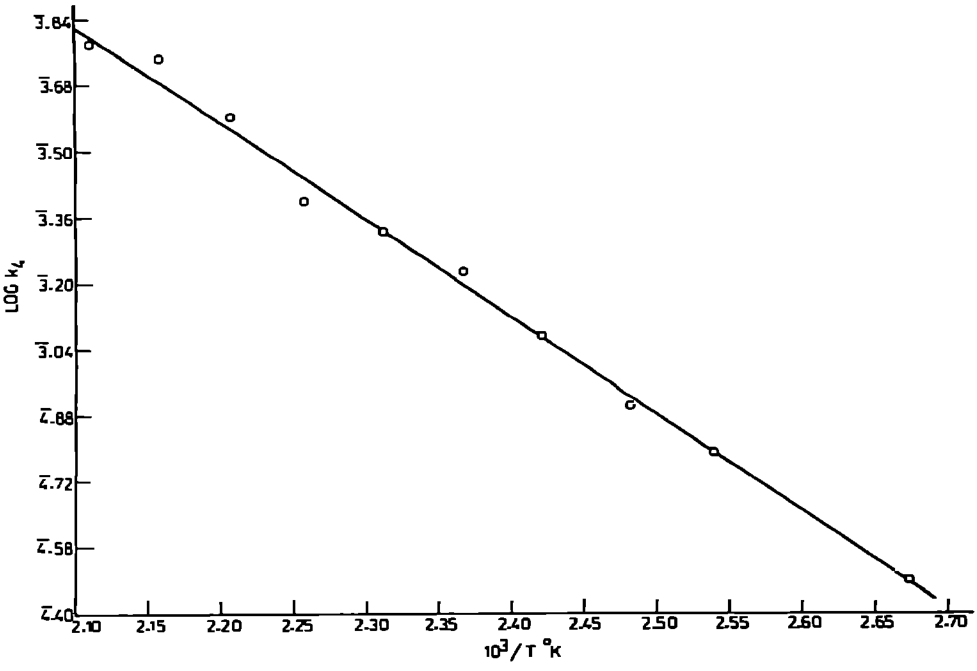


Fig. 10. Arrhenius plot of contracting-volume equation rate constants, i.e. log $k_4$ vs. $1/T \times 10^3$ (K).

decomposition could best be described by a unimolecular decay law (Fig. 7). The activation energy was determined by an Arrhenius plot (Fig. 8), and was found to be 14.4 kcal $mol^{-1}$. The contracting-volume equation is obeyed in the later stages of the decomposition (Fig. 9). Again the activation energy was determined by an Arrhenius plot (Fig. 10); the value of $E_a$ is 10.9 kcal $mol^{-1}$.

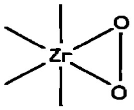
## DISCUSSION

The shapes of the $\alpha$—$t$ plots for isothermal decomposition of the two solids studied are similar to those of $K_3Zr_2(O_2)_2F_7 \cdot 2\ H_2O$ [18]. The initial part of the decomposition obeys a unimolecular decay law, which indicates rapid or instantaneous nucleation followed by rapid surface growth. By the time the surface is completely transformed into the product, sufficient penetration of the reaction zone in the particle [2,22] is also possible. The later stages of decomposition obey the contracting-volume equation, indicating that the surface is transformed into the product and the interface progresses in the direction of the centre of the particle. For the sake of comparison, activation energies obtained from Arrhenius plots are given below.

| Compound<br>$M_3Zr_2(O_2)_2F_7 \cdot xH_2O$ | Activation energies (kcal $mol^{-1}$) | |
|---|---|---|
| | Unimolecular decay law | Contracting-cube equation |
| $K_3Zr_2(O_2)_2F_7 \cdot 2\ H_2O$ [18] | 9.9 | 7.0 |
| $Rb_3Zr_2(O_2)_2F_7 \cdot H_2O$ | 13.1 | 9.7 |
| $Cs_3Zr_2(O_2)_2F_7 \cdot 2\ H_2O$ | 14.4 | 10.9 |

It can be seen that the activation energies are uniformly low in all cases, that they show a slight increase from the potassium to the caesium compounds, and that they are nowhere near to the O—O bond energy (34.0 kcal $mol^{-1}$) in magnitude. Uniformly low and comparable activation-energy values indicate that the rate-determining step, whatever it may be, seems to be common in all the solids, providing that the anion part remains the same.

The charge-transfer phenomenon is considered to be the first step in dealing with the results of thermal decomposition of ionic solids [23]; in the case of covalent compounds, perhaps the analogous step is the bond rupture. It has been observed, on the basis of laser-Raman and IR studies, that the peroxo group is triangularly-linked bidentate in nature in these solids and thus constitutes a highly strained ring system,



[16]. It is therefore probable that in these solids the first step in the peroxide decomposition is the breaking of the metal—peroxide bond and the releasing of the strain of the system. However, no data are available for

metal—peroxide bond energies for comparison. Secondly, the low activation energies for these solids may be attributed to facile nucleation followed by rapid transport of oxygen through the pores developed due to the loss of most of the lattice water before the onset of peroxide decomposition. After the cleavage of the metal peroxide bond, an extensive lattice rearrangement may be taking place with the evolution of oxygen and water, and formation of oxofluorozirconate.

$$M_3Zr_2(O_2)_2F_7 \cdot x\ H_2O(s) \rightarrow M_3Zr_2O_2F_7(s) + O_2(g) + x\ H_2O(g)$$

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